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Second law analysis of the ideal Ericsson magnetic refrigeration

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ABSTRACT

One of the main challenges of the industry today is to face its impact on global warming considering that the greenhouse effect problem is not be solved completely yet. Magnetic refrigeration represents an environment-safe refrigeration technology. The magnetic refrigeration is analysed using the second law analysis in order to obtain a model for engineering application.

Contents

1. Introduction

One of the main challenges of the industry today is to face its impact on global warming [1]; moreover, the greenhouse effect problem is not be solved completely yet. So, in addition to further developing the vapour compression technology, technical physicists and engineers have begun to explore new refrigeration technology such as magnetic refrigeration. The magnetic cooling technology is based on the use of the magnetocaloric effect (MCE) applied to various metallic materials and new alloys named magnetocaloric materials (MCM). This application uses reversible temperature change in paramagnetic salts to obtain low temperatures by adiabatic demagnetization [1]. Magnetic refrigeration is an environment-safe refrigeration technology [2]; indeed, magnetic cooling offers an innovative technical solution that will enable to reduce this global warming impact through two ways: first, it will eliminate refrigerant fluids as CFC, HCFCs and other ammonia, thus it will decrease the direct gas emissions; last, it can use the intrinsic better performance of a magnetocaloric material [1]. The magnetic refrigeration does not have ozone-depleting and greenhouse effects for employing magnetic materials as refrigeration media [2].

In 1976, Brown first applied the magnetic refrigeration in a room temperature range [3]. The magnetic refrigeration unit can be compact, for the magnetic entropy density of magnetic material is larger than that of refrigerant gas [2]. Based on the concept of the active magnetic regenerator, Zimm et al. developed a magnetic refrigerator in 1996, which used approximately 3 kg of Gd as working material and generated up to 500–600 W cooling power in a 5 T magnetic field [4].

The magnetic field of magnetic refrigeration can be supplied by electromagnet, superconductor or permanent magnet, which have no need for compressors with movable components, large rotational speed, mechanical vibration, noise, bad stability and short longevity. The efficiency of magnetic refrigeration [5] can be 30–60% of Carnot cycle [4], whereas the efficiency of vapour compression refrigeration is only 5–10% of Carnot cycle [2]. Cooling power of 110 W, temperature span of 33 °C or more between the cold sink and the hot sink [1].

In recent years, magnetic refrigeration on the basis of MCE has been greatly developed in the room temperature range. Whether

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in the range of room temperature or low temperatures, the magnitude of MCE of magnetic material is the key to cooling capacity [2]. The main research work has been dedicated to new magnetocaloric alloys that can operate in ambient temperature range from −50 °C to +65 °C [1]. After 2002 different prototypes implementing these MCM and alloys have been designed using permanent magnet systems with high field intensities.

In this paper we wish to introduce a theoretical second law analysis in a general Ericsson magnetic cycle. To do so in Section 2 we will introduce the relations on entropy, in Section 3 the second law analysis of the magnetic refrigeration and in Section 4 we will evaluate the quantities introduced for engineering application with simple approximations.

2. Entropy and entropy generation

Classical science emphasized equilibrium and stability, while, recently, it was pointed out the role of fluctuations, instability and evolutionary processes: irreversible processes are observed everywhere symmetry is broken. In thermodynamics the distinction between reversible and irreversible processes has been introduced by using the concept of entropy so that its formulation is fundamental for understanding thermodynamic aspects of self-organization, evolution of order and life that we see in Nature as it is recently pointed out [6].

The introduction of entropy in classical thermodynamics is related to equilibrium state and reversible transformation. In that context, entropy is a state function depending only on the equilibrium state of the system considered and only entropy differences can be evaluated [7]. The introduction of entropy generation comes from the necessity to avoid inequalities [9] and use only equation from mathematical point of view. Nothing is really produced [7,9–11]. Indeed, the second law states:

$$\oint \frac{\delta Q}{T} \le 0 \tag{1}$$

defining the total entropy as [8]:

$$\oint \left(\frac{\delta Q}{T}\right)_{rev} = \Delta S_e + S_g \tag{2}$$

then S_g, elsewhere called ΔS_{irr}, is considered the generated entropy and it is always $S_g \ge 0$ and defined as [11]:

$$S_g = \int_{\tau_1}^{\tau_2} \dot{S}_g d\tau \tag{3}$$

and τ_1 and τ_2 are the initial and final time of the process.

The quantity ΔS_e should be better defined as the entropy variation that will be obtained exchanging reversibly the same fluxes throughout the system boundaries. Then entropy is not more then a parameter characterizing the thermodynamic state and the term due to internal irreversibility, S_g, measures how far the system is from the state that will be attained in a reversible way [7,11,12].

Entropy is known as the fundamental quantity in the second law thermodynamics, with the following properties [13,14]:

1. the entropy of a system is a measure of the amount of molecular disorder within the system;
2. a system can only generate, not destroy, entropy;
3. the entropy of a system can be increased or decreased by energy transports across the system boundary;
4. the entropy of the state of a system is a measure of the probability of its occurrence.

The definition and identification of the thermodynamic system is fundamental. The concept of random motion was translated into a notion of order and disorder. Energy transfers or conversions are changes of the state of a system. The natural direction of a change in state of a system is from a state of low probability to one of higher probability: disordered states are more probable than ordered ones. This is the property that changes in all the energy transfers and conversions: the entropy of a state of a system depends on its probability [6].

The non-equilibrium statistical mechanics has been used in order to obtain the statistics for entropy generation in the probability space [11]. Indeed, the results obtained underlines that the relevant physical quantities for the stochastic analysis of the irreversibility are the probability of the state in the phase space, the Hamiltonian valued at the end points of trajectory, and the time [12]. Very often, all transformations refer to the same time interval and time derivative could be avoided as in classical thermodynamics [8].

3. Entropy analysis of the magnetic refrigeration

The magnetocaloric effect, which is intrinsic to all magnetic materials, indicates that the paramagnetic or soft ferromagnetic materials expel heat and their magnetic entropy decreases when the magnetic field is applied isothermally; or otherwise absorb heat and their magnetic entropy increase when the magnetic field is reduced isothermally [2].

Important characteristics of a magnetic material are its total entropy S and the entropy of its magnetic subsystem S_M (magnetic entropy). Entropy can be changed by variation of the magnetic field, temperature and other thermodynamic parameters. The entropy of magnet at constant pressure, $S(T,H)$ is magnetic field and temperature dependent; it consists of the magnetic entropy $S_M(T,H)$, both magnetic field and temperature dependent, the lattice entropy $S_L(T)$ and the electronic entropy $S_E(T)$, both only temperature dependent [5]:

$$S(T,H) = S_M(T,H) + S_L(T) + S_E(T) \tag{5}$$

Magnetic refrigerator completes cooling-refrigeration by magnetic material through magnetic refrigeration cycle. In general a magnetic refrigeration cycle consists of magnetization and demagnetization in which heat is expelled and absorbed, respectively, and two other benign middle processes.

The magnetic refrigeration ideal COP has recently been studied in [5] and it is usually defined as:

$$\mathrm{COP} = \frac{Q_0}{L} \tag{6}$$

with Q_0 the subtracted heat because of the magnetocaloric effect, and L the work done. It is useful to underline that only the magnetic entropy can be controlled by changing the strength of the magnetic field.

Some considerations have been introduced [2,5]:

1. magnetization at constant field in both paramagnets and ferromagnets decreases with increasing temperature $(\partial M/\partial T)_H < 0$;
2. large total angular momentum number J and Landè factor g of ferromagnetic material, are crucial to magnetocaloric effect;
3. modest Debye temperature;
4. modest Curie temperature in the vicinity of working temperature to guarantee that the large magnetic entropy change can be obtained in the whole temperature range of the cycle;
5. essentially zero magnetic hysteresis;
6. small specific heat and large thermal conductivity to ensure remarkable temperature change and rapid heat exchange;
7. large electric resistance to avoid the eddy current loss;
8. fine molding and processing behaviour to fabricate the magnetic materials satisfactory to the magnetic refrigeration;

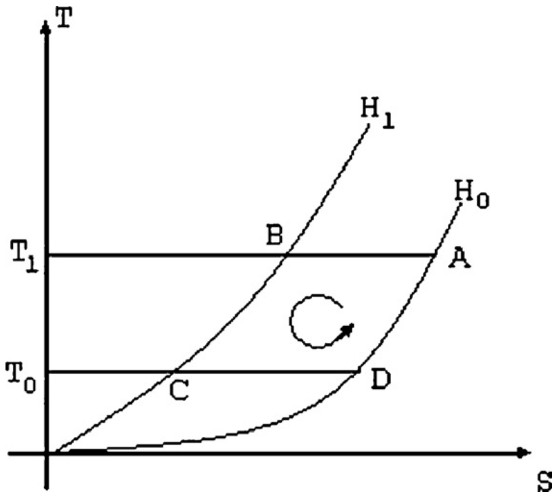

Fig. 1. Magnetic Ericsson cycle.

9. the COP depends on temperatures in non linear way;
10. it does not depend from the value of the magnetic field, but only from its variation.

Since the lattice entropy is too large to be neglected in room temperature, part of the refrigeration capacity of the magnetic refrigerant is consumed for cooling the thermal load of lattice system, decreasing the gross cooling capacity of the magnetic refrigerant [15]. By adding a regenerator to the magnetic refrigeration system, the heat expelled by lattice system in one stage of the cycle is restored and returned to lattice system in another stage. So the capacity used for cooling lattice system load can be utilized effectively for the increase of effective entropy change and temperature span.

4. Second law analysis of the Ericsson magnetic refrigeration

The magnetic Ericsson cycle (Fig. 1) consists of two isothermal processes/stages and two isofield processes:

1. isothermal magnetization process $A \rightarrow B$: when magnetic field increases from H_0 to H_1, the heat transferred from magnetic refrigerant to regenerator fluid, $Q_{AB} = T_1(S_A - S_B)$, makes the upper fluid increase in temperature;
2. isofield cooling process $B \rightarrow C$: in constant magnetic field of H_1, both magnetic refrigerant and hence electromagnet move downward to bottom and hence heat $Q_{BC} = \int_{S_C}^{S_B} TdS$ is transferred from magnetic refrigerant to regenerator fluid. Then a temperature gradient is set up in the regenerator;
3. isothermal demagnetization process $C \rightarrow D$: when magnetic field decreases from H_1 to H_0, the magnetic refrigerant absorbs heat $Q_{CD} = T_0(S_D - S_C)$ from the lower regenerator fluid. After that, the fluid decreases in temperature.
4. isofield heating process $C \rightarrow D$: in the field of H_0, magnetic refrigerant and electromagnet move upward to the top and the regenerator fluid absorbs heat $Q_{AD} = \int_{S_A}^{S_D} TdS$.

In the analysis of magnetic bodies, it is introduced the magnetization M defined as:

$$\mathbf{M} = \chi(\mathbf{H} + \mathbf{H}_{ext}) \tag{7}$$

where $\chi = C/(T - C\lambda)$ is the magnetic susceptivity, with C Curie constant, T temperature and $\lambda = TC/C = 3kT_C S(S+1)\mu^2/(Ng^2)$ constant independent of temperature, with T_C Curie temperature, k Boltzmann constant, S total spin, $g = 1 + [J(J+1) + S(S+1) - L(L+1)]/[2J(J+1)]$ Landè factor, with J total angular momentum, I orbital momentum, N number of atoms or molecules, μ Bohr magneton, and $\boldsymbol{H}$ and $\boldsymbol{H}_{ext}$ the inside and external magnetic field. Then it follows that $\boldsymbol{M} = C(\boldsymbol{H} + \boldsymbol{H}_{ext})/(T - C\lambda)$ and [5]:

$$\left(\frac{\partial M}{\partial T}\right)_H = -\frac{C(H + H_{ext})}{(T - C\lambda)^2} \tag{8}$$

and, by the Maxwell relations, we can obtain:

$$\left(\frac{\partial S_M}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H = -\frac{C(H + H_{ext})}{(T - C\lambda)^2} \tag{9}$$

which, considering the previous relations, it has been obtained [5]:

$$\left(\frac{\partial S_M}{\partial H}\right)_T = -C(H + H_{ext})[T - \Gamma]^{-2} \tag{10}$$

where

$$\Gamma = \frac{12CkT_C\mu^2 SJ^2(S+1)(J+1)^2}{N[3J(J+1) + S(S+1) - L(L+1)]^2} \tag{11}$$

Consequently, it follows:

$$\begin{aligned}
Q_{AB} &= -T_1(S_B - S_A) = -C\frac{T_1}{(T_1 - \Gamma)^2}(H_1 - H_0) \\
Q_{CD} &= -T_0(S_D - S_C) = C\frac{T_0}{(T_0 - \Gamma)^2}(H_1 - H_0) \\
L &= Q_{AB} - Q_{CD} = -C(H_1 - H_0)\left[\frac{T_1}{(T_1 - \Gamma)^2} + \frac{T_0}{(T_0 - \Gamma)^2}\right] \\
\mathrm{COP} &= \frac{Q_{CD}}{L} = \frac{1}{T_1/T_0[(T_0 - \Gamma)/(T_1 - \Gamma)]^2 + 1}
\end{aligned} \tag{12}$$

5. Conclusions

In 1881, the study of magnetic refrigeration was started with the discovery of magnetocaloric effect, when E. Warburg discovered the thermal effect of metal iron when he applied it in a varying magnetic field. P. Debye and W.F. Giauque explained the nature of magnetocaloric effect and suggested an ultra-low temperature can be achieved by adiabatic demagnetization cooling. Then it has been used in cryogenic refrigeration since 1930. In 1976, G.V. Brown applied the magnetic refrigeration in a room temperature range. Magnetic refrigeration is an environment safe refrigeration technology because it does not have ozone-depleting and greenhouse effects; in fact, it uses magnetic materials as refrigeration media. In recent years, magnetic refrigeration has been greatly developed in the room temperature range because it is understood that it may be the key of cooling capacity [5].

The entropy concept and its production in non-equilibrium processes form the basis of modern thermodynamic engineering and technical physics. Entropy has been proved to be a quantity that is related to non-equilibrium dissipative process. The second law of thermodynamics states that for an arbitrary adiabatic process the entropy of the final state is equal to (reversible process) or larger than that of the initial state, what means that the entropy tends to grow because of irreversibility. The MaxEP may be viewed as the natural generalization of the Clausius–Boltzmann–Gibbs formulation of the second law. In the last decades, the fundamental role of entropy generation has been pointed out in the analysis of

real systems and an extremum principle for this quantity has been introduced [7,11].

A second law analysis of the Ericsson magnetic refrigeration cycle has been carried out and the COP has been obtained. It follows that the COP depends on temperatures in non linear way and it does not depend from the value of the magnetic field, but only from its variation.

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